



English translation of JP-56-140933A

SPECIFICATION

5 1. TITLE OF THE INVENTION

A process for producing cymene

2.SCOPE OF CLAIM FOR PATENT

1. A process for producing cymene by a catalytic reduction
10 of dimethyl styrene with hydrogen, which comprises using a
palladium/alumina catalyst at a reaction temperature of
10-130°C, and passing upwardly a concurrent flow of dimethyl
styrene and hydrogen from the bottom layer to the top layer
of the catalyst.

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3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for producing
cymene, more particularly to a process for producing cymene
which is useful for an intermediate of synthetic cresol, by
20 catalytic reduction (hereinafter referred to
as "hydrogenation") of dimethyl styrene with hydrogen in the
presence of a palladium/alumina catalyst without substantial
reduction of the aromatic nuclei.

Methods for producing isopropyl benzene by hydrogenating
25 of α -methyl styrene which is an analogous compound of
dimethyl styrene have often been reported.

For example, in A.I.Ch.E. Journal., 1957, Sep. 366-369, a
method for using a fixed bed of palladium catalyst with

feeding hydrogen from the bottom and α -methyl styrene counter-currently from the top is disclosed. However, this method has drawbacks such as inefficiency of the catalyst due to the tendency of non-uniform flows of a reaction liquid in the catalyst layer or the shortening of the catalyst life time
5 due to the tendency of deposition of gum-like compounds produced by hydrogenation on the catalyst.

Further, the UK patent No.942, 645 specification discloses a continuous hydrogenation process in the presence of a fixed
10 bed of palladium/carbon catalyst, however, the catalyst has an insufficient mechanical strength in spite of high catalyst activity and therefore has a crucial drawback of the difficulty of catalyst regeneration.

The UK patent No.677, 091 specification also discloses a
15 process applying a nickel catalyst, however, the nickel catalyst has drawbacks compared to a palladium-based catalyst such as the tendency of generating of by-products or the difficulty of catalyst regeneration.

On the other hand, methods for producing cymene by
20 hydrogenating of dimethyl styrene have never been known at all. After various investigations of commercially superior process for producing cymene by hydrogenating dimethyl styrene avoiding the above drawbacks occurred in the production of analogous compounds, the present inventors have
25 found a process to obtain cymene economically without substantial formation of the aromatic nuclei-hydrogenated products when hydrogenation is carried out using a specific catalyst under a specific manner, and have completed the

invention.

Namely, the present invention provides a process for producing cymene by the catalytic reduction of dimethyl styrene with hydrogen, which comprises using a
5 palladium/alumina catalyst at a reaction temperature of 10-130°C, and passing upwardly a concurrent flow of dimethyl styrene and hydrogen from the bottom layer to the top layer of the catalyst.

The present invention is explained in more detail further
10 below.

In the present invention, as described above, a palladium/aluminum catalyst is used and the content of palladium in the catalyst is usually from 0.1 to 1 % by weight, preferably 0.3 to 0.5 % by weight. When the content of
15 palladium in the catalyst is less than 0.1% by weight, the lifetime of the catalyst becomes short due to the low activity of the catalyst. When the content of palladium in the catalyst is more than 1% by weight, the activity of the catalyst is so high that aromatic nuclei-hydrogenated compounds are
20 likely to produce and it is not economical from the viewpoint of catalyst cost.

The temperature of hydrogenation is preferably 10 to 130°C. When the temperature is less than 10°C, it is not economical that an excess amount of hydrogen is required due to the slow
25 reaction rate, on the other hand, when the temperature is more than 130°C, the catalyst life becomes short due to the huge increase of the aromatic nuclei-hydrogenated compounds and the tendency of producing gum-like compounds.

A pressure of hydrogenation is sufficiently not more than 10 kg/cm², and when the pressure is more than 10 kg/cm², it is not economical because aromatic nuclei-hydrogenated compounds are likely to produce and also resulting the
5 increase of equipment expense.

Dimethyl styrene as a raw material such as o-methyl- α -methyl styrene, meta and para isomers of o-methyl- α -methyl styrene or a mixture thereof can be supplied into the reaction system per se, but usually used as a dilution with
10 an inert solvent.

As the most preferable solvent used is cymene, which is the same compound as the objective compound. In case of cymene, the dilution ratio is usually about 5 to 50 times because the larger temperature difference between the inlet and outlet of
15 the catalyst layer is not preferable from the viewpoint of catalyst life.

The ratio of hydrogen used to dimethyl styrene is economically 1 to 2 times by mole when the excess hydrogen is not recycled, and is preferably 1 to 10 times by mole when
20 the excess hydrogen is recycled in order to restrict the generation of the aromatic-ring hydrogenation.

In the invention, it is essential that both dimethyl styrene and hydrogen should be supplied from the bottom to the top of the catalyst layer so that the mixtures
25 concurrently and upwardly pass the layer.

On the other hand, for example, in the case of countercurrent supply, both catalyst efficiency and catalyst yield become low.

Next, the present invention will be explained by the following examples.

5 Example 1

A mixture of cymene containing 5% of a mixed dimethyl styrene (composition ratio; *o*, α -type: *m*, α -type : *p*, α -type = 5:75:20) and hydrogen were continuously fed from the bottom of a reactor, in which 200ml of 0.3% palladium/alumina
 10 pellet was packed as a catalyst, at a rate of 1000ml/hr(liquid space velocity per hour;5) and 1.5Nl/hr(2 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. At this time, the inlet temperature of the reactor was 60°C and the
 15 outlet temperature of the reactor was 70°C, respectively, and the pressure was 2kg/cm²G. After reaching a steady state, a sample was collected from the upper portion of the reactor. The analytical values of the sample (gas chromatogram area percentage method) were as follows;

20

Mixture of cymene(%)	99.9
Mixed dimethyl styrene(%)	0.1>
Aromatic nuclei-hydrogenated products(%)	0.01

25 Example 2

A mixture of cymene containing 15% of a mixed dimethyl styrene as used in example 1 and hydrogen were continuously fed from the bottom of a reactor, in which 200ml of 0.3%

palladium/alumina pellet was packed as a catalyst, at a rate of 1000ml/hr(liquid space velocity per hour;5) and 45Nl/hr(2 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. The inlet temperature of the reactor was 100 °C and the outlet temperature of the reactor was 130°C, respectively, and the pressure was 2kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

10

Mixture of cymene(%)	99.9
Mixed dimethyl styrene(%)	0.1>
Aromatic nuclei-hydrogenated products(%)	0.1

15 Example 3

A mixture of cymene containing 5% of a mixed dimethyl styrene as used in example 1 and hydrogen were continuously fed to the bottom of a reactor, in which 200ml of 0.5% palladium/alumina pellet was packed as a catalyst, at a rate of 1000ml/hr(liquid space velocity per hour;5) and 75Nl/hr(10 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. At this time, the inlet temperature of the reactor was 30°C and the outlet temperature of the reactor was 35°C, respectively, and the pressure was 2kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

Mixture of cymene(%)	99.9
Mixed dimethyl styrene(%)	0.1>
Aromatic nuclei-hydrogenated products(%)	0.01>

5 Example 4

A mixture of cymene containing 15% of a mixed dimethyl styrene as used in example 1 and hydrogen were continuously supplied to the bottom of a reactor, in which 200ml of 0.5% palladium/alumina pellet was packed as a catalyst, at a rate
 10 of 400ml/hr(liquid space velocity per hour;2) and 18Nl/hr (2 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. At this time, the inlet temperature of the reactor was 70°C and the outlet temperature of the reactor was 85°C, respectively, and
 15 the pressure was 8kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

Mixture of cymene(%)	99.9
20 Mixed dimethyl styrene(%)	0.1>
Aromatic nuclei-hydrogenated products(%)	0.03

Comparative Example 1

A mixture of cymene containing 5% of a mixed dimethyl
 25 styrene as used in example 1 and hydrogen were continuously fed to the bottom of a reactor, in which 200ml of 2% palladium/carbon granule was packed as a catalyst, at a rate of 1000ml/hr(liquid space velocity per hour;5) and

150Nl/hr(20 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. The inlet temperature of the reactor was 120°C and the outlet temperature of the reactor was 125°C, respectively, and the pressure was 2kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

	Mixture of cymene(%)	92.2
10	Mixed dimethyl styrene(%)	0.1>
	Aromatic nuclei-hydrogenated products(%)	7.5

Comparative Example 2

A mixture of cymene containing 5% of a mixed dimethyl styrene as used in example 1 and hydrogen were continuously fed to the bottom of a reactor, in which 200ml of 0.3% palladium/alumina pellet was packed as a catalyst, at a rate of 1000ml/hr (liquid space velocity per hour;5) and 15Nl/hr (2 times by mole per mole of dimethyl styrene), respectively, so as to pass through the catalyst layer upwardly. At this time, the inlet temperature of the reactor was 150°C and the outlet temperature of the reactor was 155°C, respectively, and the pressure was 2kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

	Mixture of cymene(%)	95.8
	Mixed dimethyl styrene(%)	0.1>

Aromatic nuclei-hydrogenated products(%) 4.2

Comparative Example 3

A mixture of cymene containing 5% of a mixed dimethyl
 5 styrene as used in example 1 was downwardly and continuously
 supplied to the top of a reactor, in which 200ml of 0.3%
 palladium/alumina pellet was packed as a catalyst, at a rate
 of 1000ml/hr (liquid space velocity per hour;5), on the other
 hand, 15Nl/hr(2 times by mole per mole of dimethyl styrene)
 10 of hydrogen was upwardly and continuously supplied to the
 bottom of the reactor, as a countercurrent flow to the
 dimethyl styrene. At this time, the inlet temperature of the
 reactor was 60°C and the outlet temperature of the reactor
 was 70°C, respectively, and the pressure was 2kg/cm²G. The
 15 analytical values of the sample, which was collected after
 reaching a steady state, were as follows;

Mixture of cymene(%)	97.3
Mixed dimethyl styrene(%)	2.7
20 Aromatic nuclei-hydrogenated products(%)	0.01>

Comparative Example 4

A mixture of cymene containing 5% of a mixed dimethyl
 styrene as used in example 1 was downwardly and continuously
 25 supplied to the top of a reactor, in which 200ml of 2%
 palladium/carbon granule was packed as a catalyst, at a rate
 of 1000ml/hr (liquid space velocity per hour;5), on the other
 hand, 150Nl/hr(20 times by mole per mole of dimethyl styrene)

of hydrogen was upwardly and continuously supplied to the bottom of the reactor, as a countercurrent flow to the dimethyl styrene. At this time, the inlet temperature of the reactor was 120°C and the outlet temperature of the reactor
 5 was 125°C, respectively, and the pressure was 2kg/cm²G. The analytical values of the sample, which was collected after reaching a steady state, were as follows;

	Mixture of cymene(%)	94.6
10	Mixed dimethyl styrene(%)	0.1>
	Aromatic nuclei-hydrogenated products(%)	5.4

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PATENT ABSTRACTS OF JAPAN

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(54) PREPARATION OF CYMENE

(57)Abstract:

PURPOSE: To obtain cymene economically, by the catalytic reduction of dimethylstyrene with hydrogen in a specific temperature range passing the starting material together with hydrogen upwardly through a catalytic layer consisting of a Pd-aluminum catalyst.

CONSTITUTION: Cymene is obtained by the catalytic reduction of dimethylstyrene with hydrogen at 10W130° C in the presence of a Pd-alumina catalyst (the content of Pd in the catalyst is pref. 0.3W0.5wt%). the dimethylstyrene is passed together with hydrogen upwardly through the catalyst layer.

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⑭ シメンの製造法

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① 特 願 昭55-46089

⑯ 発 明 者 合津一志

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明 細 書

1. 発明の名称

シメンの製造法

2. 特許請求の範囲

ジメチルステンを水素接触還元してシメンを製造するにあたり、反応温度10〜130℃で触媒としてパラジウム-アルミナ触媒を使用し、かつジメチルステンおよび水素を触媒層の下部から上部に向かって共流的に上向方向に通過させることを特徴とするシメンの製造法。

3. 発明の詳細な説明

本発明はシメンの製造法に関し、更に詳しく

たとえば、A.I.Ch.E. Journal., 1957, Sep. 366〜367には、パラジウム触媒の固定床を用いて水素を下方から、α-メチルステンを上方から対向的に供給する方法が記載されているが、この方法では触媒層における液の流れが側流となり易いため触媒の効率が悪く、また水素によって生成するガム状物が触媒層に沈着し易く、触媒の寿命が短くなるという欠点がある。

また、英特許第 942,645 号明細書にはパラジウム-カーボン触媒の固定床により連続的に水素する方法が記載されているが、該触媒は酸

物が生成し易く、触媒の再生も困難であるという問題がある。

しかしながら、ジメチルステレンを水素してシメンを製造することは従来全く知られておらず、本発明者らはジメチルステレンを水素してシメンを製造すべく、かつ上記類似化合物の製造時における諸問題を生ぜしめることなく工業的に有利にシメンを製造すべく種々検討の結果、特定触媒を使用し、かつ特定方法で水素することにより、加水分解物が実質的に生成することなく有利にシメンが製造し得ることを見出し、本発明に至った。

すなわち本発明は、ジメチルステレンを水素化触媒としてシメンを製造するにあたり、反応温度 $10\sim130^{\circ}\text{C}$ で触媒としてパラジウム-アルミナ触媒を使用し、かつジメチルステレンおよび水素を触媒層の下部から上部に向かって逆流的に上向方向に通過させることを特徴とするシメンの製造法である。

以下、本発明について詳細に説明する。

系に供給することも可能であるが、通常は反応に不活性な溶媒で希釈して用いられる。かかる溶媒として最も好適なのは生成物と同じシメンであって、この場合の希釈割合は触媒の寿命から考えて触媒層の入口、出口の温度差をあまり大きくすることは好ましくないため、通常 $5\sim50$ 倍程度である。

ジメチルステレンに対する水素の使用量は、過剰水素を再使用しない場合には $1\sim2$ 倍モル使用するのが経済的であり、過剰水素を再使用する場合には加水分解物の生成を抑制するため $1\sim10$ 倍モル程度が適当である。

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本発明は前記したようにパラジウム-アルミナ触媒を使用するものであるが、該触媒中のパラジウム含量については通常 $0.1\sim1$ 重量%、好ましくは $0.3\sim0.5$ 重量%である。含量が 0.1 重量%未満では触媒活性が低いため触媒寿命が短くなり、 1 重量%を越えると触媒活性が過剰なため加水分解物が生成し易くなる傾向があり、また触媒の価格も高くなって経済的でない。

水素温度は $10\sim130^{\circ}\text{C}$ が適当であり、 10°C 未満では反応速度が遅いため大過剰の水素が必要のため、経済的でなく、 130°C を越えると加水分解物が飛躍的に増加すると共にガム状物質も生成しやすくなり、触媒寿命の低下をきたす。

水素圧力は 10 kg/cm^2 以下で十分であり、 10 kg/cm^2 を越えると加水分解物が生成しやすくなりまた設備費も増加するため経済的でない。

原料ジメチルステレンたとえば α -メチル- α -メチルステレンまたはこの α -、 β -異性体あるいはこれらの混合物は、これ単独で反応

実施例1

0.3% パラジウム-アルミナベレット 20 ml を充填した反応塔の下部から混合ジメチルステレン（組成比 α 、 α 体： β 、 β 体： γ 、 α 体： $5:75:20$ ） 5% を含む混合シメン 1000 ml/hr （毎時液体空間速度 5 ）および水素 15 ml/hr （ジメチルステレンに対するモル比 2 ）を触媒層を上向方向に通過するように連続的に供給した。この時反応塔の入口温度は 40°C 、出口温度は 70°C であり圧力は 2 kg/cm^2 であった。定常状態に達した

有する混合シメン 1000 ml/Hr (毎時液体空間速度 5) および水素 4.5 NL/Hr (ジメチルステレンに対するモル比 2) を触媒層を上向方向に通過するように連続的に供給した。反応塔の入口温度は 100℃、出口温度は 130℃であり、圧力は 2 kg/cm² であった。定常状態に達したあと採取したサンプルの分析値は下記の通りであった。

混合シメン(%)	混合ジメチルステレン(%)	脱水炭化物(%)
99.9	0.1 >	0.1

実施例 3

0.5g パラジウム-アルミナベレット 200 ml を充填した反応塔の下部から、実施例 1 で用いたと同じ混合ジメチルステレン 5g を含有する混合シメン 1000 ml (毎時液体空間速度 5) および水素 7.5 NL/Hr (ジメチルステレンに対するモル比 10) を触媒層を上向方向に通過するように連続的に供給した。この時反応塔の入口温度は 30℃、出口温度は 35℃であり、圧力は 2 kg/cm² であった。定常状態に達したあと採取したサンプルの分析値は下記の通りであった。

200 ml を充填した反応塔の下部から、実施例 1 で用いたと同じ混合ジメチルステレン 5g を含有する混合シメン 1000 ml (毎時液体空間速度 5) および水素 150 NL/Hr (ジメチルステレンに対するモル比 20) を触媒層を上向方向に通過するように供給した。反応塔の入口温度は 120℃、出口温度は 125℃であり、圧力は 2 kg/cm² であった。定常状態に達したあと採取したサンプルの分析値は下記の通りであった。

混合シメン(%)	混合ジメチルステレン(%)	脱水炭化物(%)
92.2	0.1 >	7.8

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図に示したあと採取したサンプルの分析値は下記の通りであった。

混合シメン(%)	混合ジメチルステレン(%)	脱水炭化物(%)
99.9	0.1 >	0.01 >

実施例 4

0.5g パラジウム-アルミナベレット 200 ml を充填した反応塔の下部から、実施例 1 で用いたと同じ混合ジメチルステレン 5g を含有する混合シメン 400 ml (毎時液体空間速度 2) および水素 1.5 NL/Hr (ジメチルステレンに対するモル比 2) を触媒層を上向方向に通過するように連続的に供給した。この時反応塔の入口温度は 70℃、出口温度は 85℃であり、圧力は 5 kg/cm² であった。定常状態に達したあと採取したサンプルの分析値は下記の通りであった。

混合シメン(%)	混合ジメチルステレン(%)	脱水炭化物(%)
99.9	0.1 >	0.03

比較例 1

2g パラジウム-カーボンダニユール

反応塔の入口温度は 150℃、出口温度は 155℃であり、圧力は 20 kg/cm² であった。定常状態に達したあと採取したサンプルの分析値は下記の通りであった。

混合シメン(%)	混合ジメチルステレン(%)	脱水炭化物(%)
95.8	0.1 >	4.2

比較例 3

0.3g パラジウム-アルミナベレット 200 ml を充填した反応塔の上部から実施例 1 に使用したと同じ混合ジメチルステレン 5g を含有する混合シメン 1000 ml/Hr (毎時液体空間速度 5) を下向方向に連続的に供給し、一方、

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混合シメン(%) 混合ジメチルステレン(%) 炭水素物(%)

97.3

2.7

0.01 >

比較例4

2号パラジウム→カーボングラニユール
200 μ mを充填した反応塔の上部から実験例に
使用したと同じ混合ジメチルステレン5%を
含有する混合シメン1000 ml/hr（毎時反応体空
間速度5）下向方向に連続的に供給し、一方、
流量150 ml/hr（ジメチルステレンに対する
モル比20）を反応塔の下部からジメチルス
チレンと対向的に上向方向となるように連続
的に供給した。この時の液入口温度は120℃、
出口温度は125℃であり、圧力は2 $\times 10^5$ Paで
あった。定常状態に達したあと採取したサンプ
ルの分析値は下記の通りであった。

混合シメン(%) 混合ジメチルステレン(%) 炭水素物(%)

94.6

0.1 >

5.4